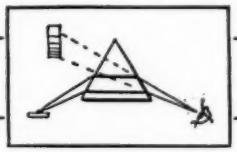
Journal of the OPTICAL SOCIETY *of* AMERICA

VOLUME 25
No. 10



OCTOBER
1935

Radiation and Absorption of Energy by Tungsten Filaments at Low Temperatures . . . . IRVING LANGMUIR AND J. BRADSHAW TAYLOR 321

Photo-Electromotive Forces and Currents in Single Crystals of Selenium . . . . . R. M. HOLMES 326

Back Numbers Wanted 329

Optimum Grain Size in the Christiansen Filter . . . . . H. S. DENMARK AND WILLOUGHBY M. CADY 330

Integrating Factor of the Photometric Sphere . . . . FRANK BENFORD 332

Simplified Computation of Cartesian Lens Surfaces . . LUDWIK SILBERSTEIN 340

Photoelectric Colorimeter with Logarithmic Response . . . . . RALPH H. MÜLLER AND GILBERT F. KINNEY 342

Apparatus for Darkfield Photometry and Densitometry . . . . . P. S. WILLIAMS AND GORDON H. SCOTT 347

Published monthly
at Prince and Lemon Sts., Lancaster, Pa.
by the
AMERICAN INSTITUTE OF PHYSICS
Incorporated
11 East 38th Street, New York, N. Y.
FOR AND UNDER THE EDITORIAL SUPERVISION OF
THE OPTICAL SOCIETY OF AMERICA

THE OPTICAL SOCIETY OF AMERICA

OFFICERS OF THE SOCIETY

W. B. RAYTON, *President*
Bausch & Lomb Optical Company
Rochester, New York

ARTHUR C. HARDY, *Vice President*
Massachusetts Institute of Technology
Cambridge, Massachusetts

L. B. TUCKERMAN, *Secretary*
Bureau of Standards
Washington, D. C.

HENRY F. KURTZ, *Treasurer*
Bausch & Lomb Optical Company
Rochester, New York

The Board of Directors consists of the above officers; the Editor of the Journal; the Past President; and five elected members:

E. C. CRITTENDEN, *Past President*
Bureau of Standards
Washington, D. C.

F. K. RICHTMYER, *Editor*
Cornell University
Ithaca, New York

Elected Members

ARTHUR H. COMPTON
Ryerson Physical Laboratory
University of Chicago
Chicago, Illinois

HERBERT E. IVES
463 West Street
New York, New York

CARL W. KEUFFEL
Keuffel & Esser Company
Hoboken, New Jersey

GEORGE B. PEGRAM
Columbia University
New York, New York

R. C. GIBBS
Department of Physics
Cornell University
Ithaca, New York

THE OPTICAL SOCIETY OF AMERICA was organized in 1916 *"to increase and diffuse the knowledge of optics in all its branches, pure and applied, to promote the mutual interests of investigators of optical problems, of designers, manufacturers and users of optical instruments and apparatus of all kinds and to encourage cooperation among them."* It aims to serve the interests of all who are engaged in any branch of optics from fundamental research to the manufacture of optical goods.

MEMBERSHIP

Regular Members: "Any person who has contributed materially to the advancement of optics is eligible for regular membership."

Associate Members: "Any person who is interested in optics is eligible for associate membership."

Corporate Members: "Any corporation desirous of encouraging the work of the Society is eligible for corporation membership."

The Society cordially invites to membership all who are interested in any branch of optics, either in research, in instruction, in optical or illuminating engineering, in the manufacture and distribution of optical goods of all kinds or in physiological and medical optics.

ANNUAL DUES

Regular members, $7.50; Associate members, $5.00; Corporate members, $50.00. These dues include subscription to the Society's official journal, the *Journal of the Optical Society of America.*

MEETINGS

The Society holds two meetings per year: An annual meeting in the autumn and a midwinter meeting jointly with the American Physical Society.

For further information concerning the Optical Society of America address the Secretary, Dr. L. B. Tuckerman, Bureau of Standards, Washington, D. C.

ROCHESTER, NEW YORK SECTION OF THE OPTICAL SOCIETY OF AMERICA

C. C. NITCHIE, *President*
H. E. SEEMANN, *Secretary*

L. A. DUBRIDGE, *Vice President*
H. G. KINGSLAKE, *Treasurer*

Councilors: E. C. FRITTS, R. KINGSLAKE, H. F. KURTZ, T. R. WILKINS, C. J. STAUD (*ex-officio*)

Journal of the
OPTICAL SOCIETY
of AMERICA

VOLUME 25 OCTOBER, 1935 NUMBER 10

Radiation and Absorption of Energy by Tungsten Filaments at Low Temperatures

IRVING LANGMUIR AND J. BRADSHAW TAYLOR, *Research Laboratory, General Electric Company*

(Received July 17, 1935)

The radiation of energy from a thoriated tungsten filament and the absorption of the energy radiated from the surrounding bulb have been measured by a method which eliminates difficulties arising from cooling effects of the leads. For a filament at a uniform temperature T_F in a bulb at temperature T_B the net radiation W in watts cm^{-2} is the difference between the outgoing radiation W_R and the absorbed radiation W_A. For values of T_F from 225° to 580°K and T_B from 77° to 473°K

$$\log W_R = 83.7105 - 100 + 5.332 \log T_F,$$
$$\log W_A = 83.7105 - 100 + 4.462 \log T_B + 0.87 \log T_F.$$

The resistivity R_0 in this same range is given by

$$\log R_0 = 91.7123 - 100 + 1.23 \log T_F.$$

The characteristics, current, voltage, resistance, and energy radiated as functions of temperature are tabulated.

IN some studies of the adsorption of cesium on thoriated tungsten filaments which are now in progress in this laboratory, it has become necessary to know accurately the relation between the temperature at the midpoint of the filament and the heating current. In much of this work it is desired to operate at filament temperatures which only slightly exceed the bulb temperature.

Although published tables [1,2] of the characteristics of tungsten filaments have given the relation between the watts input and the temperature even for low filament temperatures, these data have not been the result of direct experiment, but have been calculated with somewhat doubtful accuracy from assumed values of the emissivity of tungsten. In view of the present need for greater accuracy, it is thus seen desirable to undertake experimental determinations of the radiation from tungsten filaments at low temperatures and of the absorption of the energy radiated back from the bulb.

Let W be the net radiation from the filament in watts per square cm. This is the difference between the outgoing radiation W_R and the absorbed radiation W_A, so that

$$W = W_R - W_A. \qquad (1)$$

Let E be the total emissivity, that is, the ratio between W_R and the radiation from the filament if it behaved like a black body. Thus

$$W_R = ST_F^4 E, \qquad (2)$$

where S is the Stefan-Boltzmann constant, 5.72×10^{-12} watt per cm^2 deg.^{4}. In this equation T_F is the absolute temperature of the filament.

The absorbed radiation W_a is given by the equation

$$W_A = ST_B^4 A, \qquad (3)$$

where A is the absorption coefficient for the

[1] I. Langmuir, Phys. Rev. **7**, 302 (1916).

[2] H. A. Jones and I. Langmuir, Gen. Elec. Rev. **30**, 310, 354, 408 (1927).

BOSTON UNIVERSITY
COLLEGE OF LIBERAL ARTS
LIBRARY

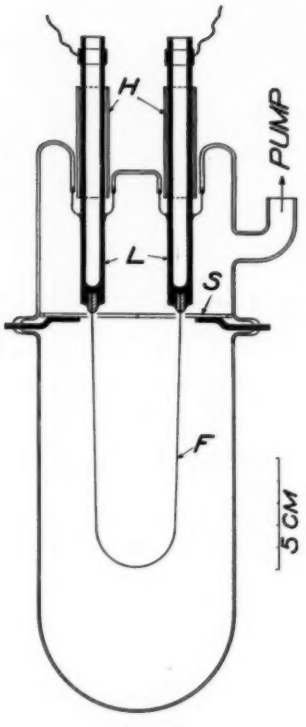


FIG. 1.

incident radiation upon the filament, and T_B is the bulb temperature.

P. Foote[3] extended some previous calculations by Aschkinass based on Drude's theory of metals, and obtained the equation

$$E=0.5736(TR_0)^{\frac{1}{2}}-0.1769(TR_0), \qquad (4)$$

where R_0 is the specific resistance of the filament material which is at the temperature T.

In this derivation, however, E was calculated as the emissivity of radiation in the direction normal to the surface of the filament. Davisson and Weeks[4] made much more elaborate calculations taking into account the deviations from Lambert's law, and thus obtained for E the expression

$$E=0.751(TR_0)^{\frac{1}{2}}-0.632(TR_0)+0.670(TR_0)^{\frac{3}{2}}-0.607(TR_0)^2\cdots. \qquad (5)$$

A is given by the same expression if T is replaced by T_B.

Davisson and Weeks made careful measurements of E for platinum for temperatures up to 1500°K. Between 300 and 500°K they obtained values of E from 10 to 14 percent lower than those calculated by Eq. (5). At values above 700°, however, they observed that the values of E were greater than the calculated values.

One of the greatest difficulties of making measurements of radiation at low filament temperatures arises from the cooling effect of the leads. In the present experiments it was decided to eliminate this difficulty by providing means of heating the leads to the temperature at which the filament is operated. The apparatus used is shown in Fig. 1. The leads (L) consisted of heavy walled copper tubing, of an outer diameter of 11 mm and an inner diameter of 8 mm, closed at one end, into which gold buttons carrying the filament (F) were silver soldered in vacuum. The gold buttons had been fused around the filament in hydrogen, thus making good thermal and electrical contact. The leads were silver soldered in vacuum to copper cups which had previously been sealed to the Nonex glass bulb. A thermometer and also a thermocouple were placed in the bottom of the opening of the tubular lead. The heat conductivity of the copper was so great that no appreciable temperature difference could exist between the thermometer bulb and the gold button which was in contact with the filament. The leads were heated by means of resistance wire furnaces (H) placed around that portion of the copper above the seal. In certain experiments the leads were cooled by immersing heavy copper strap extensions of the leads in liquid air. Polished nickel plates (S), making contact with the bath liquid through heavy seals, shielded the filament from the radiation of the leads and the upper exposed parts of the bulb.

A thoriated tungsten filament (~1.2 percent of thoria) was used having a diameter of 0.00499 cm as calculated from the weight, assuming the density of tungsten to be 19.31 after thorough aging. The length of the filament between the gold buttons was 25.82 cm. In aging the filament, its temperature was raised in steps of about 50° every five minutes to 2000°K and held here

[3] P. Foote, Bull. Bur. Stand. **11**, 607 (1915).
[4] C. Davisson and J. R. Weeks, Jr., J. O. S. A. **8**, 581 (1924).

for fifteen minutes. In thoriated tungsten this initial treatment produces a particularly fine grained filament. Photomicrographs of lengthwise sections showed the average grain diameter to be about 0.002 mm. The filament was now heated at 2400°K for four hours and at 2600° for one hour, followed by a few short flashes at 2800 and 2900°K. Further heating at 2600 to 2800°K during the experiments caused no change in resistance or emissivity. The bulb was baked out and was kept connected to the pump and McLeod gauge. The pressure during the measurements was less than 10^{-6} mm.

The relation between the resistance of the filament and the temperature was determined by heating the entire bulb and the leads to a series of different temperatures in an oil bath. Thus, when no current is passed through the filament, the bulb temperature T_B, the lead temperature T_L and the filament temperature T_F were equal. In order to measure the resistance, a small current I was passed through the filament, and the voltage drop across the filament was determined, both measurements being made with high accuracy by a potentiometer. Measurements of resistance were obtained with several values of current I, and these resistances were plotted against I^2, and the intercept of the resulting straight line corresponding to $I=0$ was obtained. This resistance should therefore correspond to the bulb and lead temperature. These tests were made with the bulb evacuated; and to be sure no temperature differences existed between bulb, leads, and filament, they were checked after admitting dry hydrogen at atmospheric pressure.

The resistivity is given by

$$\log R_0 = 91.7123 - 100 + 1.230 \log T. \quad (6)$$

The slope, 1.23, of the log resistance log temperature relation is about halfway between the values given by Langmuir and Jones[2] (approximately 1.26) and that found recently (1.209) by Forsythe and Watson.[5] The values of resistivity are from 1 to 2 percent higher than reported by either of these authors. This may be caused by the thoria content of the present filament; however, Forsythe and Watson mention differences as great as 6 percent in pure tungsten filaments from different sources. In no case has this difference in resistivity caused differences in radiating properties.

To determine the radiation characteristics of the filament, the leads were maintained at various temperatures T_L, above the bulb temperature T_B. Knowing what the resistance of the filament should be at the temperature T_L, we passed a current through the filament sufficient to bring the resistance to this value. Actually, currents slightly above and slightly below this value were used and the observed energy in watts per cm², W, was plotted against R. By interpolation the value of W was found which corresponded to a filament temperature T_F which was the same as lead temperature T_L.

Measurements were made in this way of the net radiation W for a series of 8 bulb temperatures ranging from that of liquid nitrogen (~77°) to 473°K, while the lead and filament temperatures were adjusted at a large number of values from 225 to 580°K.

With the tube in liquid nitrogen the radiation received by the filament from the bulb is negligible, and so W measured under these conditions is equal to W_R. It was found that $\log W_R$ plotted against $\log T_F$ gave a straight line of slope 5.332, so that

$$\log W_R = 83.7105 - 100 + 5.332 \log T_F. \quad (7)$$

The experimentally determined points lay along this straight line within a maximum error of 0.3° and an average error of less than 0.1°.

The agreement of the experimental data with Eqs. (6) and (7) indicates that between 230° and 600°K both the resistance and the outward radiation vary accurately in proportion to definite powers of T_F.

Thus we may put

$$R_0 = \text{const } T_F^{\rho}, \quad (8)$$

where $\rho = 1.230$, and

$$W_R = KT_F^{\omega}, \quad (9)$$

where K is a constant and $\omega = 5.332$.

Foote and Davisson and Weeks[3, 4] suggest that A is a function of (R_0T_B) while E is the same function of (R_0T_F), and thus both A and

[5] W. E. Forsythe and E. M. Watson, J. O. S. A. **24**, 114 (1934).

E are expressible as proportional to powers of T_F and T_B. Comparing Eqs. (2) and (9) we see in fact that

$$E=(K/S)(T_F)^{\omega-4}. \tag{10}$$

We are thus led to the tentative assumption that A can be expressed by

$$A=\text{const } T_F^{\epsilon}T_B^{\alpha}, \tag{11}$$

where ϵ and α are constants.

When $T_F=T_B$, $W=0$ and thus by Eqs. (1), (2), and (3), $A=E$. This condition requires, according to Eqs. (10) and (11), that

$$\omega-4=\epsilon+\alpha \tag{12}$$

and

$$A=(K/S)T_B^{\omega-4}(T_F/T_B)^{\epsilon}. \tag{13}$$

Inserting the values of E and A from Eqs. (10) and (13) into Eqs. (2) and (3) and combining with Eq. (1) gives

$$W=K(T_F^{\omega}-T_B^{\omega-\epsilon}T_F^{\epsilon}). \tag{14}$$

We have subjected this equation to experimental test. We wished to know particularly whether the assumption of Eq. (11) is justified. In other words, are the values of ϵ determined from the experiments really constant when both T_B and T_F are varied? For this purpose we transformed Eq. (14) into the following form,

$$\log (W_R-W)-\log W_B = \epsilon(\log T_F-\log T_B), \tag{15}$$

where W_B, the outward radiation from the filament when it is at bulb temperature T_B, is to be found by Eq. (7) by replacing T_F and W_R by T_B and W_B, respectively.

The experiments in which T_F and T_B are different gave values of W as a function of T_F and T_B. According to Eq. (15) if $\log (W_R-W)-\log W_B$ is plotted as ordinate with $\log T_F-\log T_B$ as abscissa, all the points should lie on a single straight line of slope ϵ which passes through the origin. The experimental data gave complete agreement with this theory and gave the value $\epsilon=0.87$.

The deviations of the points given by the experimental data from the straight line were such as could be explained by errors in the lead temperatures. In most cases they were less than 0.3°, but in a few cases where the accuracy of the control of the lead temperatures was known to be less, a few errors of 1 or 2° were observed. There was no tendency for deviations that suggest that ϵ varies progressively with either T_B or T_F, and therefore we may regard the assumption underlying Eq. (11) as being justified experimentally.

TABLE I. *Total emissivity of tungsten.*

T_F	E L and T	E D and W	Ratio
300	0.0179	0.0301	1.68
400	.0262	.0410	1.56
500	.0353	.0520	1.47
600	.0450	.0629	1.40

Our experimental determinations of W_A, the energy absorbed as back radiation, are therefore completely represented by the equation

$$\log W_A=83.7105-100+4.462 \log T_B +0.87 \log T_F. \tag{16}$$

By then finding W_R by Eq. (7) and inserting these values into Eq. (1) the net radiation W can be calculated for a tungsten filament at a uniform temperature T_F in a bulb at temperature T_B.

According to the theory of Davisson and Weeks, the emissivity E can be expressed as a function of R_0T_F, while A is the same function of R_0T_B. This would imply that A should be a function of $T_F^{1.23}\,T_B$ only. Actually, from Eq. (13), after inserting the numerical values of ω and ϵ, we find that A is a function of $T_F^{1.88}\,T_B$ or $R_0^{1.53}\,T_B$.

The values of the emissivity E which we have found are given by

$$\log E=4.9531-10+1.332 \log T_F. \tag{17}$$

The second column of Table I gives values of E calculated by this equation. The third column gives values calculated by the Davisson and Weeks relation, Eq. (5).

The reflection of radiation of sufficiently long wave-length from metals can undoubtedly be calculated by the electromagnetic theory by methods similar to those used by Davisson and Weeks. At 300°K the wave-length corresponding to the maximum radiant energy is about 10μ, while at 1500°K it is 2μ. Since the Davisson and Weeks equation gives emissions which show the

TABLE II. *Characteristics of tungsten filaments.*

T_F (°K)	$W' \times 10^4$ (watts cm^{-2})	$R' \times 10^6$ (ohms cm)	A' (amp. cm^{-1})	$V' \times 10^6$ (volts cm^{-1})	T_F (°K)	$W' \times 10^4$ (watts cm^{-2})	$R' \times 10^6$ (ohms cm)	A' (amp. cm^{-1})	$V' \times 10^6$ (volts cm^{-1})
230	6.3145	5.2744	10.942	57.712	400	120.72	10.418	34.04	354.63
240	7.8795	5.5578	11.907	66.177	410	137.70	10.739	35.808	384.54
250	9.8496	5.8439	12.983	75.871	420	156.59	11.062	37.624	416.20
260	12.140	6.1327	14.070	86.287	430	177.53	11.387	39.485	449.62
270	14.846	6.4241	15.202	97.659	440	200.67	11.713	41.391	484.81
280	18.024	6.7181	16.378	110.029	450	226.21	12.042	43.342	521.92
290	21.733	7.0144	17.602	123.47	460	254.35	12.372	45.342	560.97
300	26.037	7.3131	18.869	137.99	470	285.26	12.703	47.388	601.97
310	31.012	7.6140	20.182	153.67	480	319.13	13.037	49.471	644.95
320	36.733	7.9177	21.540	170.55	490	356.25	13.372	51.615	690.20
330	43.280	8.2226	22.943	188.65	500	396.74	13.708	53.798	737.46
340	50.751	8.5302	24.392	208.07	520	489.00	14.385	58.303	838.69
350	59.235	8.8400	25.886	228.83	540	598.00	15.069	62.995	949.27
360	68.832	9.1515	27.426	250.99	560	726.02	15.758	67.879	1069.6
370	79.660	9.4654	29.01	274.59	580	875.41	16.454	72.941	1200.2
380	91.831	9.7807	30.642	299.70	600	1048.80	17.154	78.192	1341.3
390	105.49	10.099	32.32	326.40					

$W' = W/Ld$, $R' = Rd^2/L$, $A' = A/d^{3/2}$, $V' = Vd^{1/2}/L$, where W, R, A, and V are the observed values of watts input, resistance, current, and voltage for a filament of length L cm and diameter d cm at the uniform temperature T_F when surrounded by walls at 0°K.

greatest deviations at the lowest temperatures, it is evident that the wave-length of 10μ is still far too small for the application of the classical theory of metals.

Forsythe and Watson[5] have recently made accurate experimental determinations of W_R above 600°K. Below 600°, since they made no measurements of back radiation, they could only estimate values of W_R. Our values obtained by direct experiment are about 20 percent lower than these estimated values of Forsythe and Watson. If our log W_R-log T relation is extended from 600°K with a slope of 5.58 instead of 5.332, it passes midway between W_R as given by Forsythe and Watson and by Jones and Langmuir and joins their values as they come into good agreement at about 1000°K.

For general calculations it is convenient to follow the procedure of Jones and Langmuir[2] and to tabulate the characteristics of tungsten in terms of a filament of unit (1 cm) length and diameter. In Table II, the resistance R', the watts input (net energy radiated) W', the current A', and the voltage V' are given for a filament at the uniform temperature T_F, when surrounded by walls at 0°K. The table can be used directly for calculating temperatures only when these conditions are fulfilled.

Ordinarily the bulb is not at a temperature sufficiently low to make W_A negligible, and the distribution of temperature and other properties is not uniform along the filament because of the cooling effects of the leads. The calculation of temperatures for these conditions with a newly determined value for the heat conductivity of tungsten will be described in a following paper.

Photo-Electromotive Forces and Currents in Single Crystals of Selenium

R. M. HOLMES, *University of Vermont*

(Received June 14, 1935)

PHOTO–E.M.F'S. in selenium photo-resistance cells have been observed by many investigators. The most recent studies of the photo-e.m.f. obtained with this element have been made in Germany with cells generally consisting of a thin layer of selenium on a disk of iron, a translucent film of some metal being deposited on the surface of the selenium. When light is incident on the film an electron current flows from the film through an outside circuit and returns to the iron disk without the necessity of a source of e.m.f. in the outside circuit. The details of the methods of preparing these cells are not given.

The present article is concerning the photo-e.m.f's. and currents in single crystals of selenium with electrodes of translucent platinum films. No work on single crystals has been published. Since the degree of purity and state of crystallization of selenium in any form other than that of a single crystal are open to considerable doubt it is believed that work with single crystals is significant.

PREPARATION OF CRYSTALS. APPARATUS

The single crystals were grown by a method essentially as described by Brown.[1] Briefly, the selenium at a temperature of about 280°C was contained in the bottom of a Pyrex tube held vertically in an electric oven with automatic temperature control. Selenium vaporized in the lower end of the tube and condensed on the walls of the tube and on a Pyrex fiber hanging in the center. The crystals were thus formed from the vapor phase and were located in a region at a temperature between 200°C and 215°C. However, the exact conditions under which crystals grow are not known as is evident from the fact that many attempts at crystal growth are failures. Work along this line is now being done. However, when the vapor is sufficiently free from impurities to allow selenium atoms to arrange themselves in regular crystal formation one may be sure that the single crystals so formed are of a very high degree of purity.

Nearly all of the crystals were of the acicular type. The number of lamellar or flat crystals was small but the work to be described was done with lamellar crystals. These were perfectly flat with mirror like surfaces up to 75 sq. mm in area and with thicknesses in the vicinity of 0.12 mm. A sheet of polycrystalline selenium of these dimensions is so brittle that it is very difficult to work with it. The single crystals, however, are quite strong and easy to handle.

Translucent platinum films were deposited on each of the two flat surfaces by cathodic sputtering. The area of the films was regulated by use of a sheet of mica with a rectangular opening placed over the crystal in the sputtering jar. This allowed the deposit of a film of the desired area and prevented the films on the two surfaces from overlapping around the edges of the crystal. The film deposited on the mica shield allowed an estimate to be made of the percentage transmission of light. The sputtering was done very slowly and with rectified current to minimize heating.

After the films had been sputtered the crystal was mounted between microscope slides, fine platinum wires serving as leads to the platinum films. The cell was exposed to light from a tungsten lamp operated by a storage battery the radiation being incident normally on one of the films. The long wave-length radiation was always removed by filtering through circulating tap water. When it was desired to expose the cell to light confined to a narrow region of the spectrum the method of isolating narrow spectral regions by means of filters as described by Jones[2] was used. When an equal energy spectrum was needed use was made of a Coblentz thermopile and low resistance galvanometer.

The current from the cell was measured with a galvanometer and the opposing p.d. which was introduced into the circuit to reduce the gal-

[1] F. C. Brown, Phys. Rev. **4**, 85 (1914).

[2] L. A. Jones, J. O. S. A. **16**, 259 (1928).

vanometer current to zero was measured with a potentiometer arranged in the usual manner.

Results

When the platinum leads were connected to the current measuring system without a source of e.m.f. in the outside circuit, light on one of the platinum films caused an electron current to flow from selenium to platinum at the illuminated surface. The variation of the current (I) in the outside circuit with illumination (L) is shown for a typical case in Fig. 1. This crystal had a surface area of 75 sq. mm and a thickness of 0.13 mm. The films had areas of 35 sq. mm each and the deposits on the mica shield indicated that the films absorbed about 40 percent of the incident light. The curve is plotted by using values of illumination on the platinum film allowance being made only for absorption by the water cell. The resistance in the galvanometer circuit was small relative to the internal resistance of the photo-e.m.f. cell. Fig. 1 also shows the opposing p.d. necessary in the outside circuit to reduce the current to zero. By analogy with voltaic cells this will be referred to as the e.m.f., E, of the photo-e.m.f. cell.

To study the effects of different wave-lengths and to demonstrate that the current is not thermoelectric the cell was exposed to an equal energy spectrum. Fig. 2 shows the current with no outside e.m.f. and with negligible external resistance. This figure also shows the photo-e.m.f. A filter combination allowing exposure to a band of approximately 7000A was not available. However, the decrease of photo-current and of photo-e.m.f. to zero for radiation near the red end of the visible spectrum has been verified in other ways. For example, by using a thin layer of molybdenite which absorbs all visible radiation but which transmits a band between 10,000A and 14,000A a very small current was obtained in the reverse direction. The radiation transmitted by the molybdenite filter had energy equal to that of the equal energy spectrum of Fig. 2.

Fig. 3 shows the resistance, R, of the photo-e.m.f. cell measured under illumination and with an outside source of 4.3 volts e.m.f. The photo-e.m.f. is so small relative to the e.m.f. of the outside source that the former is negligible. The resistance of the cell in the dark was 0.30 megohm. The resistance under the strongest illumination used was about one-fifteenth of the dark value. This is a very high resistance change

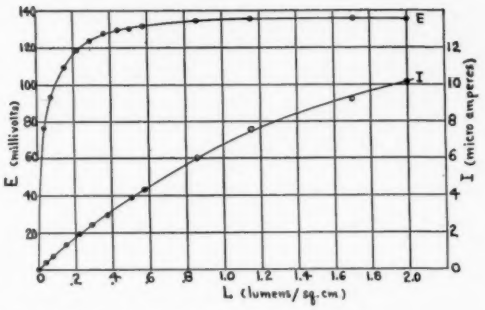


Fig. 1. Current, I, and e.m.f., E, from selenium crystal photo-e.m.f. cell for various illuminations.

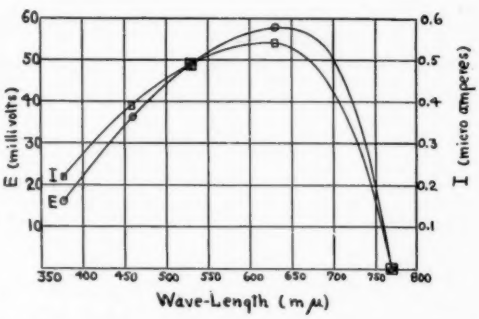


Fig. 2. Current, I, and e.m.f., E, from selenium crystal photo-e.m.f. cell for various wave-lengths using an equal energy spectrum.

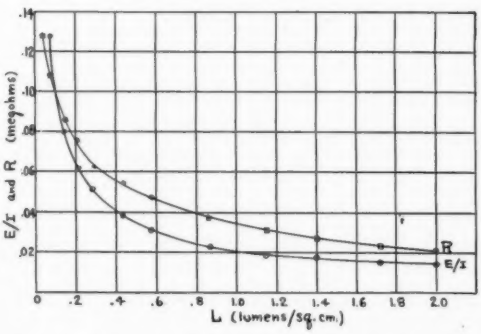


Fig. 3. Resistance, R, of selenium crystal photo-e.m.f. cell using an outside source of e.m.f. Quotient E/I where E and I are values shown in Fig. 1.

and so far as is known it is the largest photo-resistance effect so far reported for a single crystal of selenium. The magnitude of this effect is doubtless due to the thinness of the crystal and the consequent penetration of light into nearly all of the current path. Rectification effects were nearly absent. The two electrodes were nearly identical—a condition likely to result in no rectification. Fig. 3 also shows the quotient E/I. The photo-cell behaves somewhat like a voltaic cell. However, for feeble illumination E/I is somewhat greater than R while for strong illumination E/I is less than R.

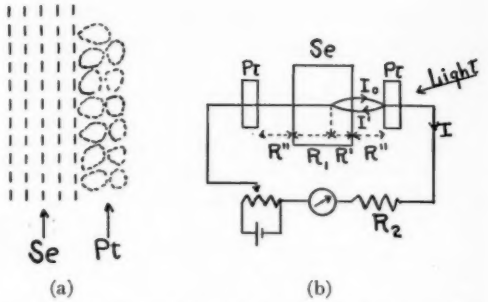


FIG. 4 (a). Representing the granules of platinum making poor contacts with the surface of the selenium crystal. (b) A simplified and diagrammatic representation of the divided circuit of the photo-e.m.f. cell. This figure shows electron current directions.

DISCUSSION

The current and e.m.f. in the case of these selenium crystals must be photoelectric. With selenium in its purest form and with no substance in contact with it other than pure platinum there is no possibility of a photochemical effect. According to *International Critical Tables* the threshold wave-lengths for polycrystalline selenium are from 2200A to 2670A while corresponding values for platinum are 2600A to 2800A. The wave-lengths used with the selenium crystals were up to 7700A. The most likely conclusion is that the presence of the platinum film very close to the surface of the selenium lowers the photoelectric work function for the selenium. Since a photoelectron emerging from selenium would have an electrical image in the platinum it seems plausible that the work done to remove the electron from the surface of the selenium would be decreased. It may be that photo-electrons are emitted from both selenium and platinum but there is evidently a greater number leaving the selenium as is shown by the fact that the electron current was always against the direction of the incident light.

The situation may be represented diagrammatically by Fig. 4(a). A sputtered platinum film consists of granules of platinum rather loosely adhering to the surface on which they are deposited. Before such a film is heat treated the granules makes rather poor electrical contacts with the surface. Light transmitted through the film evidently causes the ejection of photo-electrons from selenium, these electrons being received by platinum. In Fig. 4(b) the platinum films are represented by the smaller rectangles separated for convenience from the larger rectangle representing the selenium crystal. I_0 is the photoelectron current from selenium to platinum. I' is the electron current returning by conduction through the contacts between granules of platinum and the selenium surface while $I=I_0-I'$ is the current in the outside circuit. R' represents resistance in the selenium encountered by the electron current, I', in returning to the mean depth below the surface from which photo-electrons were ejected. R'' represents resistance of contacts between platinum granules and selenium surface. R_1 is resistance between the nonilluminated surface of the crystal and the above-mentioned mean depth from which photo-electrons are ejected. R_2 is the external resistance.

If an opposing p.d., E, is introduced in the circuit sufficient to reduce I to zero, then $E=I_0(R'+R'')$. While I_0 should be proportional to light intensity, L, it is evident that I_0 will be reduced by the opposing p.d. and also that R' will be decreased because of the photo-resistance effect. The equation for E is checked qualitatively by determining the effect of temperature.[3] As the temperature is increased from -20°C to 100°C the value of E decreases. The selenium crystals have a negative temperature coefficient of resistance. The decrease in E is accounted for since R' will decrease as temperature increases. The temperature may be changed cyclically between these limits with reversible changes in

[3] Holmes and Whitman, Phys. Rev. **47**, 337A (1935).

E. No permanent change has been made in the structure of the platinum films. However, if the films are exposed to a temperature of 180°C there is a permanent decrease in E. Upon return to room temperature E is only about one-third of its former value. This is accounted for by the well-known effect of heat treating a platinum film after it has been deposited by sputtering. As a result of heating, the granules of platinum are brought into much better contact with the selenium surface with a consequent decrease in R'' which is permanent. The e.m.f. of the cell still decreases with increasing temperature because of the variation of R' with temperature.

When there is no e.m.f. in the outside circuit the current I_0-I' will flow through the galvanometer and will return to the selenium. If I_0 is proportional to illumination the following equation may be obtained by application of Ohm's law:

$$I=kL(R'+R'')/(R_1+R_2+R'+2R'').$$

This result is also checked qualitatively by temperature effects. As the temperature is increased from -20°C to 100°C there is a reversible decrease in I. This is interpreted as being caused by the decrease in R' as the temperature is increased. If the equation be differentiated partially with respect to R' it will be seen that decreasing R' should decrease I. After the films have been exposed to a temperature as high as 180°C there is a permanent decrease in I. Differentiation of the equation partially with respect to R'' shows that the permanent decrease in R'' caused by heat treatment should cause a decrease in I provided R' is smaller than R_1+R_2.

Back Numbers Wanted

THE Optical Society of America will pay one dollar per copy for each of the following issues, unbound and in good condition:

Volume 18, No. 2—February, 1929
Volume 18, No. 5—May, 1929
Volume 19, No. 1—July, 1929
Volume 19, No. 2—August, 1929
Volume 19, No. 5—November, 1929

The notice which appeared in the July issue of this journal resulted in the purchase of a sufficient supply of the other copies listed therein.

Copies should be addressed to the American Institute of Physics, 11 East 38th Street, New York, New York, with the name and address of sender and with a covering letter.

Optimum Grain Size in the Christiansen Filter

H. S. DENMARK AND WILLOUGHBY M. CADY, *Clark University*

(Received June 18, 1935)

The width at half-maximum of the band transmitted by a Christiansen filter has been measured for ten wave-lengths, and for glass grains of six sizes in ethyl salicylate. With a cell 7.5 mm thick, the grain size affording the narrowest bands was found to be about 0.7 mm, depending somewhat upon wave-length. Bands have been observed in the violet, having a width at half-maximum as narrow as 8 to 10A, the transmission at peak being about 40 percent.

WHEN a coarse powder of annealed glass or other homogeneous isotropic transparent substance is thoroughly wetted, in a transparent cell with parallel faces, with a liquid having, for a certain wave-length λ_c, a refractive index equal to that of the powder, then light λ_c is transmitted by the cell without deviation. For $\lambda \neq \lambda_c$, the indices will in general differ. Thus only a narrow spectral band is undeviated; this light can be brought to a focus. The cell is known as a Christiansen filter.[1, 2, 3]

The transmitted wave-length λ_c varies with the temperature of the cell, by virtue of the unequal thermal coefficients of refractive index of the two components. If the dispersions are very unequal, then λ_c is less sensitive to temperature variations, and extremes of temperature are required if the filter is to be useful over any considerable range of wave-lengths. In the present investigation, the cell contained optical glass (n_D 1.523) and ethyl salicylate; λ_c varied from 5730 to 4330A within the temperature range from 22 to 57°C.

The optical system consisted of a "point" source of light (*viz.*, an incandescent lamp behind a hole 0.17 mm in diameter), the cell in a water thermostat, a projection achromat (F=65 cm) immediately outside the thermostat, and a Hilger E3 spectrograph with Wratten and Wainwright panchromatic plates. The thickness of the cell was 7.5 mm; this was not varied. The cell, 10 cm in diameter, with a circular diaphragm to limit its effective diameter to 3.7 cm, was placed at the optimum position, mid-way between the source and the slit of the spectrograph, on which the filtered light was accurately focused.

The glass was prepared by pulverizing with a hammer, cleaning chemically, sorting by differential screening, and annealing for three days at 190°C. The sizes of the particles were estimated by averaging the dimensions of the rectangular interstices in the wire screens used in sorting, which were as follows: 0.215×0.199 mm; 0.092×0.088 mm; 0.047×0.039 mm; 0.026×0.023 mm; 0.021×0.018 mm; 0.017×0.013 mm.

At each of ten temperatures (i.e., at each of ten values of λ_c) and with each of six grain sizes, five exposures were made on the same plate, the intensities being progressively diminished by factors of 2.0 with the aid of a rotating sector. Densitometer traces of any successive pair of these five exposures gave at once the band width at a half-maximum, without further need for calibrating the plate. Thus for each grain size and wave-length, several (ideally four) values of the band width were calculated; these were averaged.

Similarly, by matching filtered against unfiltered spectra, a determination of the transmission of the filter at λ_c has been made.

TABLE I. *Band width (in Angstroms) at half-maximum, as a function of grain size and wave-length.*

d (mm)	4300	4400	4500	4600	4800	5000	5200	5400	5600	5800
1.49	8.0	8.8	9.8	11.2	14.5	18.4	23.0	28.4	34.3	—
0.67	8.4	9.4	10.4	11.6	14.2	17.2	20.8	24.8	29.1	33.7
.67C	8.7	9.6	10.8	12.0	14.6	17.6	20.8	24.4	28.0	31.8
.67A	8.6	9.3	10.1	11.0	13.4	16.2	19.4	23.0	26.9	30.9
			(40%)							
.33	—	10.8	11.4	12.3	14.9	18.5	23.0	28.4	34.4	41.4
			(36%)							
.33A	10.3	11.6	13.0	14.4	17.6	21.1	24.9	28.8	32.8	37.0
			(36%)							
.22	—	10.6	12.0	13.5	17.2	21.6	26.8	33.2	40.6	49.2
.17	—	—	—	16.5	20.2	25.5	32.2	40.2	49.2	59.0

[1] Christiansen, Wied. Ann. **23**, 298 (1884); **24**, 439 (1885).

[2] Elvegard, Staude and Weigert, Zeits. f. physik. Chemie **B2**, 149 (1929).

[3] von Fragstein, Ann. d. Physik **17**, 22 (1933).

Table I gives, in Angstroms, the band width at half-maximum for several grain sizes and wave-lengths. The observations "A" were made with batches of glass that had not been annealed after crushing; it would seem that this annealing is not necessary. The observations "C" were made with a batch handled as usual, to check the reproducibility of the measurements. The transmission at the peak of the band when at 4500A is given in parentheses under the corresponding width.

The band widths at quarter- and eighth-maximum have been determined. They average, respectively, 1.46 and 1.92 times the homologous half-maximum widths, the factors being slightly greater for narrow than for wide bands.

It seems from Table I that the optimum grain size in the cell as used is about 0.7 mm, being larger for the violet. The band is wider in the yellow than in the violet, because the dispersions of the liquid and glass are more nearly equal in the yellow.

McAlister[4] has stated that a reduction of the grain size (or an increase of cell thickness) decreases the width of the band. This is evidently not true if the glass is finely pulverized and the cell is used as above described. The light source for McAlister's filter may have been rather extended, which fact, increasing the band width, would also change the dependence thereof upon grain size.

From the somewhat extended quantitative results of other recent investigators, we may choose, for comparison with our Table I, the data of Table II. It appears that, with proper precautions, the filter used as above gives superior performance.

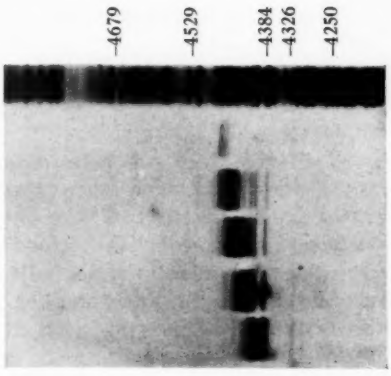


FIG. 1. Iron arc, with and without Christiansen filter

TABLE II. *Previous performances of Christiansen filters.*

OBSERVER	(A)	WIDTH (A) AT HALF-MAX.	TRANSMISSION
E. S. and W.[2]	4400	40	10.5%
von Fragstein[3]	3680	60	62%

Fig. 1 shows a small part of an iron arc spectrum. The successive exposures are: unfiltered arc; filtered arc, cell at 48.1°C; and filtered arc, longer exposures, cell at 49.0, 49.7, 50.6, 51.8°C. The short filtered exposure exhibits well how selective a monochromator can be constructed on the Christiansen principle.

[4] McAlister, Smithsonian Misc. Coll. **93**, No. 7 (1935).

The Integrating Factor of the Photometric Sphere

FRANK BENFORD, *Research Laboratory, General Electric Company*

(Received May 21, 1935)

ONE of the unsolved problems connected with spherical photometry is the production of a nonselective sphere paint. A very considerable amount of thought and effort has been devoted to this subject, as is evidenced by the numerous references in the literature, but seemingly there has not yet been obtained a paint that fulfills the exacting requirements of this particular science. The integrating action of the sphere greatly amplifies any nonuniformity in the spectral reflecting factors of the paint, and with the recent great extension in the production of lamps with marked spectral characteristics these variations in the action of the sphere are increasingly important.

At the present time those photometric laboratories that photometer incandescent lamps of various sizes must be provided with a set of standards that correspond in size with the lamps to be tested. The reason for this multiplicity of standards is not that a given sphere will not "integrate" a large quantity of light with the same "constant" as a small quantity, but because the color temperatures of lamps vary with size, and a test lamp at 2800°K cannot always be measured in terms of a standard lamp of, say, 2400°K.

If a perfectly nonselective paint were available, it would be necessary to provide each sphere with only a single standard lamp, and differences in the outputs of the test lamps could then be taken care of by simple mechanical devices, such as diaphragms and sectored disks, with a resulting great simplification of the present situation. Lacking such a paint, the best alternative seems to be to devise a method of correctly evaluating the paint under working conditions.

The experiments here reported upon have been made on a special sphere paint that has been used in several photometric laboratories, and this paint has been a success as regards stability and durability, but as will be considered in detail later, it leaves much to be desired when dealing with the wide variety of spectra encountered in present-day lamps. (See Fig. 1.)

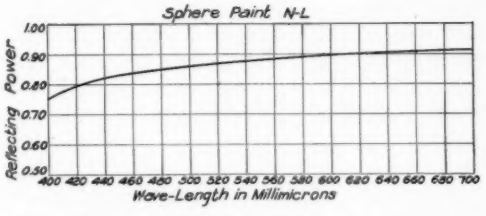


FIG. 1. Spectrophotometric analysis of the paint used in these tests. This paint has a marked drop in reflecting power in the blue and violet regions, but to the eye it seems to be pure white.

Experience with the method here described shows that a high degree of photometric and mechanical accuracy is required if dependable results are to be obtained, and for this reason considerable study has been devoted to finding working conditions that promote accurate determination of the integrating factors for various sources of light.

TYPES OF SPHERES

There are in common use at least three mechanical types of photometric integrators. Perhaps the most common, and for the present purpose, the simplest, is the sphere with a small section of wall that is hinged to swing outward and permit the insertion of a standard or test lamp. A second type of sphere is divided into equal hemispheres, one of which rolls on a track so that the two parts may be separated for the entrance of the operator. The third type separates into hemispheres, which are hinged together, so that one hemisphere may be swung open. (See Fig. 2.)

The test data given later were taken on the third type which is the most complicated to handle mathematically, and there will be a considerable saving in computations for those photometrists fortunate enough to work with the two first types. In nearly every case the form of the equation for types one and two will be somewhat simpler, and generally the simplification will be fairly evident, so that extended

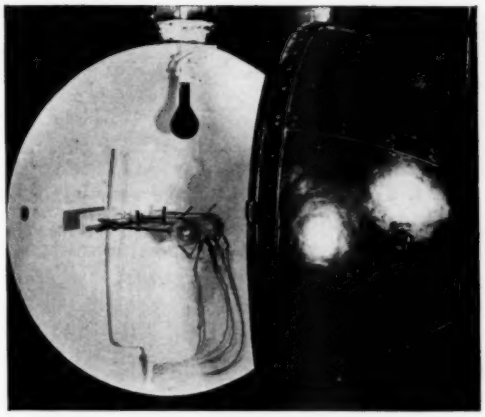


FIG. 2. An integrating sphere equipped for testing a sodium arc. The dark incandescent lamp over the sodium arc has an amber bulb and gives light that visually matches the arc in color for routine calibration. The amount of equipment required for this work adds to the difficulty of getting accurate data.

specific mention of the first two forms will be omitted.

EQUIPMENT AND METHODS

The sphere used in these experiments is 54 inches in inside diameter. It separates into hemispheres and one of the hemispheres swings on a vertical hinge so that free access may be had for the purpose of adjusting the lamps, lamp holder and screens that are part of the normal equipment of an integrating sphere. This instrument is in constant service measuring arc lamps under development, and provisions are necessary for accommodating a variety of lamps that differ widely in size, shape and electrical connections. These various "foreign bodies" complicate the theory of the sphere, and have made it necessary to pay considerable attention to test methods so that routine photometry can be carried out with sufficient accuracy, and without the use of complicated corrections.

In any sphere there are surfaces that differ in reflecting properties from the sphere paint, and for this reason a spectrum analysis of the paint never gives quite sufficient data for a computation of the integrating factor. This is particularly so in the photometry of arc lamps that are of large size and require large shields and much wire inside the sphere. These additional surfaces are often selective in a different manner than is the sphere paint, and a dependable method of computing the corrections from paint data seems to the writer to be out of the question.

Experiments have been carried out for about a year on a determination, by direct test as far as possible, of the true integrating factor of the instrument under any given condition, and coupled with this investigation is the development of a test system that effectively eliminates the questions that arise from color in the photometry of the sodium arc.

The test method of determining the effective coefficient of the sphere complete with test and standards lamps and all the necessary accessories, consists in taking photometric readings with the sphere closed and then opened a measured amount. The area of the sphere when opened is increased by the area of the opening, and the coefficient of the sphere is now a composite of the normal coefficient of the paint and a zero coefficient over the imaginary surface of the opening. The ratio of the two readings gives data for the computation of the effective coefficient of the complete instrument, as distinguished from the coefficient of the paint, and from this effective coefficient the integrating factor can be computed. This test must be made for each type of lamp that shows strong spectral characteristics, and in the case of tests on tungsten lamps of different temperatures, the determination must cover the range of operating color temperatures.

COMPUTATION OF THE EFFECTIVE COEFFICIENT

A distinction must be made between the coefficient of paint on a flat surface and on the inner surface of the sphere. The theory of the sphere depends upon the paint being a complete diffuser, but we know that no surface is perfect in this respect. If any of the so-called complete diffusers are inspected for reflection near the grazing angle they will be found sensibly to approach specular action, and there is possibly a change in spectral characteristic under the same conditions. It seems probable that sphere paint will follow the general rule of an increasing heterochromatic coefficient near grazing inci-

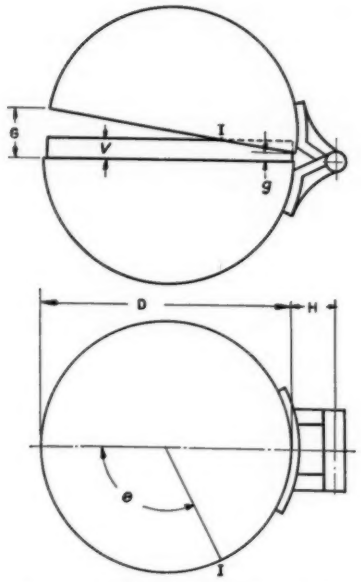


FIG. 3. Diagrammatical sketches of the sphere in partially opened and closed positions. The opened sphere permits light to escape through a wedge-shaped opening into the black photometer room.

dence, and m_p, the coefficient on a plane surface, will differ from m, the coefficient in an empty sphere.

If the sphere contains lamps, shield, wires, etc., a third coefficient m_r will exist, and finally, if the sphere is opened so that light can escape there is the coefficient m_o for the open sphere. We are chiefly concerned here with m and m_o, as these two coefficients correspond to actual working conditions.

The sphere in which these tests were made has an overlapping flange (V, in Fig. 3) one inch wide between hemispheres, and for the first inch of motion in opening the sphere there is an increase in the white area, and further opening allows the light to escape into a dark room.

Setting the area S of the closed sphere equal to unity, the flange area, w, is equal to 0.018.

The proportional area of the opening b that has been most commonly used is 0.058, and the total area S_o of the open sphere accordingly is $1.076S$ as computed from the relation

$$S_o=(1+w+b)S. \tag{1}$$

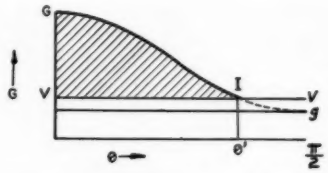


FIG. 4. Diagrammatic sketch of the area of the sphere opening. The height to the line V represents the width of white sphere wall uncovered by the flange, and the height to the curved line represents the linear opening between hemispheres.

The coefficients of the open (m_o) and closed (m) spheres are

$$m_o=(1+w)m/(1+w+b). \tag{2}$$

The brightness of the closed sphere can be written

$$B'=Fm/S(1-m), \tag{3}$$

where F is the quantity of light generated by the lamp. (See Fig. 4.) For the open sphere

$$B_o'=Fm_o/S_o(1-m_o), \tag{4}$$

where the area S_o includes the new white and black areas exposed when the sphere is opened. In this equation there is also the assumption that the surface of the sphere and the surface of the opening receive direct radiation in strict proportion to their areas. This, in practice, means that the light source should be so oriented that neither a maximum nor a minimum intensity is directed toward the opening.

The ratio R of the photometer readings, open to closed, as derived from Eqs. (3) and (4) is

$$R=N(1-m)/E(E-Nm), \tag{5}$$

where
$$N=1+w \tag{6}$$

and
$$E=1+w+b. \tag{7}$$

This determination of the relative brightness of the sphere therefore involves a determination of the two geometrical factors N and E, and the photometric ratio R.

Solving for m, the effective coefficient of the complete sphere under working conditions we get

$$m=\frac{(1-E^2R/N)}{(1-ER)}. \tag{8}$$

The relative brightness of the sphere (putting

S and F both equal to unity) is

$$B=m/(1-m) \tag{9}$$

$$B_o=Nm/E(E-Nm). \tag{10}$$

The coefficient m that has been used in the preceding equations should be defined as the effective coefficient when the foreign material in the sphere is reduced to a minimum. With a small standard lamp and a single small screen as the only foreign bodies the sphere may be considered empty, and m is used throughout to indicate this condition.

When the test lamp and its auxiliary equipment lead to a measurable absorption of light, the computation of m must take this absorption into account.

Let the ratio of the brightness B_r of the equipped sphere to the brightness B of the empty sphere be K, that is

$$B_r/B=K, \tag{11}$$

then the coefficient m of the empty sphere can be computed from the coefficient m_r of the equipped sphere by the relation

$$m=m_r/(K+(1-K)m_r). \tag{12}$$

This correction has been made in the tabulation of effective values of m that will be given later. The reverse computation of m_r when m and K are known can be made by the equation

$$m_r=Km/(1-(1-K)m). \tag{13}$$

It should be noted that the use of Eq. (12) to get the empty sphere factor does not give a correction to be applied to the sphere reading to compensate for absorption losses. The determination of m permits a correction to be made for any variations due to the spectral peculiarities of the paint, but corrections for absorption must still be made in the usual manner.

If the sphere on which the determination is being made has a door that opens so that the light may escape into a dark room, or be absorbed by a black covering over the inner surface of the door, the above equations take a slightly different form. As before, let b be the added black area, which in this case is gained by subtracting from the white area. $b+w=1$.

The size of the sphere is unaltered and

$$S_o=S. \tag{1a}$$

Also

$$m_o=wm, \tag{2a}$$

$$R=w(1-m)/(1-wm), \tag{5a}$$

$$m=(w-R)/w(1-R), \tag{8a}$$

$$B_o=wm/(1-wm). \tag{10a}$$

There are corresponding changes in the sensitivity equations, but for a given small area changed from white to black in a sphere of constant size the sensitivity will approximate the sensitivity when an identical black area is added by increasing the size of the sphere.

Computation of Factors N and E

The values of N and E may be computed with sufficient accuracy by the methods to be given, provided the opening does not form too big a percentage of the original sphere area. Test data will later be given to show how this particular sphere reacts to separation of the hemispheres. If the degree of opening is kept always the same by using some sort of gauge, then any small error in computing areas will cancel out, and comparisons between paints, or between light sources may be accurately made.

Let D = inside diameter of sphere
H = distance from sphere wall to hinge
g = opening between hemispheres, next to hinge
G = opening between hemispheres, opposite to hinge
V = depth of internal flange
θ = angle measured in plane of opening
w = white area added by opening sphere
b = black area added by opening sphere.

There is an internal flange covering the crack between the hemispheres, so that at the beginning of opening the sphere grows by the addition of the white surface that this flange covered, and it is not until the opening is greater than the depth of flange at the point farthest from the hinge that black area is added. Fig. 3 illustrates the geometrical arrangement. Assuming the black area to be a cylinder joining the edges of the separated hemispheres, the black area added is

$$b=D\int_0^{\theta_1}\left[\frac{G+g}{2}+\frac{(G-g)\cos\theta}{2}-V\right]d\theta, \tag{14}$$

where θ is measured from the horizontal axis passing through the center of the sphere, and having its zero position at the point of initial (and maximum) opening. The integration is carried to the angle θ_1 where the plane of the swinging hemisphere cuts the edge of the internal flange.

From Fig. 3 we can derive the expression for the limiting angle θ_1;

$$\theta_1=\cos^{-1}[(2V(H+D)-G(2H+D))/GD]. \quad (15)$$

Integrating and substituting limits we get

$$b=(D/2)[(G+g-2V)\theta_1+(G-g)\sin\theta_1], \quad (16)$$

where θ_1 is expressed in radians.

The white area added is

$$w=\int_0^{\theta_1} DV\,d\theta+(D/2)\int_{\theta_1}^{\pi}[(G+g)+(G-g)\cos\theta]d\theta \quad (17)$$

and, from this we derive

$$w=DV\theta_1+(D/2)[(G+g)(\pi-\theta_1)-(G-g)\sin\theta_1]. \quad (18)$$

Sensitivity and Accuracy

The final results of the method here outlined for determining the effective coefficient of the paint, and the integrating factor of the sphere, must have a relatively high accuracy if they are to be useful, and an experimental examination has been made to determine the needed accuracy in the factors, m, N, E, and B.

The sensitivity of B with respect to m can be derived from Eq. (10).

$$C_{Bm}'=mdB_o/B_o dm=E/(E-Nm) \quad (19)$$

for the open sphere, and, from Eq. (9),

$$C_{Bm}=mdB/Bdm=1/(1-m) \quad (20)$$

for the closed sphere.

In Fig. 5 the curve for the closed sphere shows the photometric reading B to vary nine times as fast as m (when $m=0.89$), so that a one percent change in m will produce a nine percent change in B under working conditions. When testing for m with an open sphere a one percent change in m causes only a six percent change in the photometric reading. The accuracy

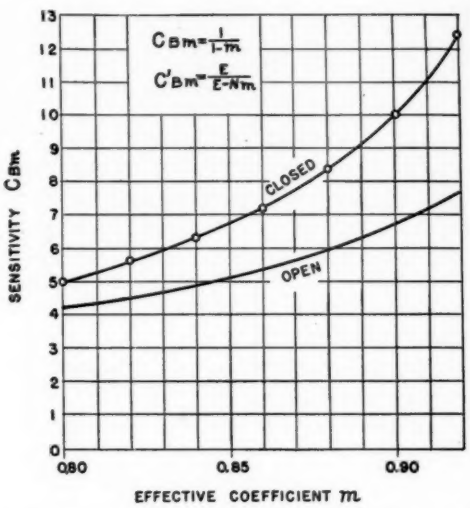


FIG. 5. Sensitivity of the sphere to variations in the coefficient m. The difference in the ordinates of the two curves represents the loss of sensitivity when testing with the sphere in the open condition. $N=1.018$, $E=1.076$.

of determination of B (or the sphere constant) as influenced by the accuracy in photometer readings, is only two-thirds of the photometric accuracy of the test. This is a much more favorable condition than exists when the paint is tested independently, as on a flat surface, for then the computed value of B varies about nine times as much as the test values of the paint for a single reflection. The advantage of this test method is therefore about six to one over the flat-sample method.

If the factor E is taken as the variable the sensitivity of the photometer reading is

$$C_{PB}=EdB_o/B_o dE=(2E-Nm)/(E-Nm). \quad (21)$$

The sensitivity to errors in measuring E is high, as illustrated in Fig. 6. Under the conditions of test a variation of one percent in E caused a variation of seven percent in the photometer reading. The factor E is equal to $1+w+b$, and the black area b had the value of 0.058, so that to make a one percent error in E it is necessary to make a 20 percent error in measuring b. It thus appears that only moderate accuracy is needed in measuring and maintaining b.

An independent check on possible errors arising from the assumption made in computing

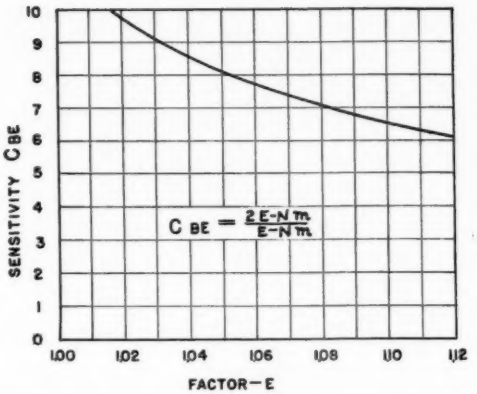


FIG. 6. Sensitivity of the sphere to variations in the factor E. When $N=1.018$, $m=0.887$. The data in this curve are of assistance in selecting a size of opening that will give the most accurate determination of the integrating factor of the sphere.

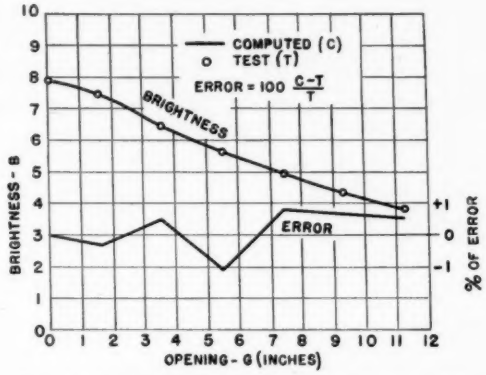


FIG. 7. Brightness of the open sphere *vs.* maximum opening G. The opening of the sphere, at the point of maximum separation, was extended to more than eleven inches without the introduction of any detectable systematic error.

the factor E was made for the value of E up to twice the value used during the other tests. An incandescent lamp was maintained at constant voltage while photometric readings were taken for various values of G up to 11.25 inches (b up to 9.44 percent). Eq. (4) for B_o was then used to compute the brightness for the same openings, with the results illustrated in Fig. 7. The data of the two determinations were of course arbitrarily brought into agreement for the $G=0$ condition, and the other differences were then computed. The average error (which should be divided between the two determinations), is seen in Fig. 7 to be about one-half of one percent, and there is no sign of a systematic failure of Eq. (4) for the larger openings.

This indicates that a black area of more than 5.8 percent could have been used in the other tests, with a gain in accuracy, or a saving in the number of photometer readings.

Errors made in determining R, the ratio of readings with an open sphere to those with a closed sphere, are not amplified when computing m. The sensitivity equation is

$$C_{Rm}=mdR/Rdm$$
$$=m(E-N)/(1-m)(E-Nm) \quad (22)$$

and, as shown in Fig. 8, R changes about three times as fast as m. Thus a one percent error in determining R leads to a one-third of one percent

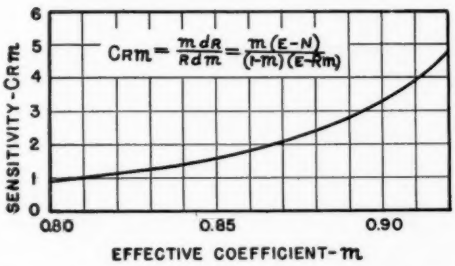


FIG. 8. Sensitivity of the ratio R for variations in the effective coefficient m. The sensitivity of this feature of the method keeps pace with the increasing sensitivity of the instrument as the coefficient m rises. $N=1.018$, $E=1.076$.

error in m, and about a three percent error in computing B, which is proportional to the sphere constant.

After the completion of a series of open-and-shut tests made to determine m and B for tungsten at various temperatures, a second independent test was made over the same temperature range. A tungsten lamp was placed in the bar photometer and held at 2347°K color temperature while the comparison lamp was brought to a color match. The comparison lamp was then held constant in voltage while the test lamp was photometered at temperatures from 2033°K to 2815°K. The color conditions were, of course, far from favorable for good photometry, but fairly consistent readings were obtained.

The test lamp was then placed in the sphere

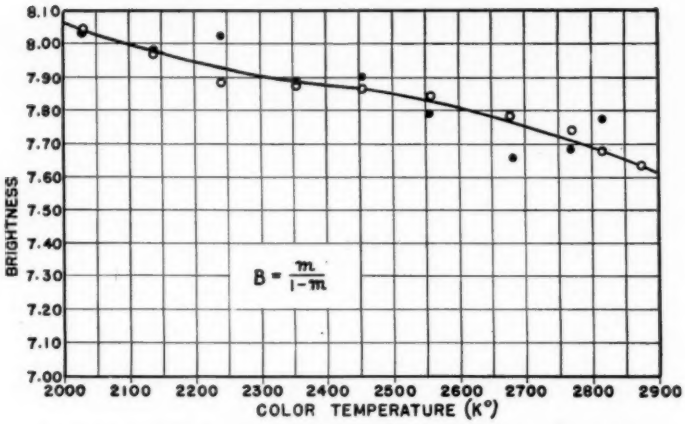


FIG. 9. Relative brightness of the sphere. The computed results by the open-and-shut method were checked by an independent method of somewhat lower inherent accuracy. Paint $N-L$. Open circle—by open-and-shut method; closed circle—by comparison with bar photometer.

and the comparison lamp was color matched with the test lamp at 2347°K. The photometer field was brought to approximately the same brightness as on the bar photometer, and the other details of the first test were duplicated as far as possible. The data of the two methods are given in Fig. 9. The comparison between the bar photometer and the sphere gives the same general trend in the temperature-brightness relation, but the accuracy of this test is not good enough for comparison with the details of the curve given in Fig. 9.

This bar-photometer method, with certain alterations, seems suitable for obtaining the temperature-brightness curve, but it is not evident how this procedure could be used for the various types of gaseous conductor arcs.

In Fig. 10 the variations in the energy composition of the mercury arc are illustrated diagrammatically. The energy values for the four main groups of lines at 4046A, 4350A, 5461A, and 5780A are connected by straight lines to bring out more clearly the great change in color that this arc may undergo as the temperature and vapor pressure are changed. Another type of mercury arc, not here illustrated, has an extremely high vapor pressure, with a correspond-

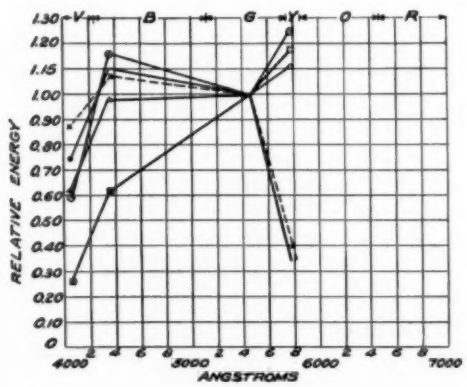


FIG. 10. Line spectra of various mercury arcs at four wave-lengths. The families of mercury lines for each type of lamp are connected by lines to bring out more clearly the wide variations in color of this type of arc. Solid circles—uviarc at low pressure; open circles—uviarc at high pressure (arc only); broken line—low pressure; triangles—$S-1$ (arc only); squares—high intensity.

TABLE I.

SOURCE	EFFECTIVE COEFFICIENT	RELATIVE INTEGRATING FACTOR
Tungsten 2000°K color temperature	0.8898	1.025
" 2200°K " "	0.8882	1.009
" 2400°K " "	0.8874	1.000
" 2600°K " "	0.8867	0.993
" 2800°K " "	0.8853	0.980
High pressure mercury arc (quartz)	0.877	0.905
Optimum " " " (glass)	0.884	0.968
Extra high " " " (quartz)	0.871	0.857
Sodium arc (plus neon)	0.888	1.006
Amber colored sodium standard	0.887	0.996
Neon arc	0.891	1.037

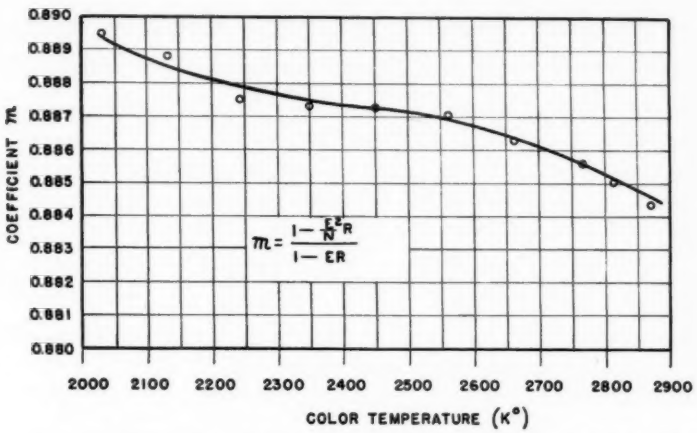


FIG. 11. The coefficient of reflection of the complete integrating sphere. The curve shows how the effective coefficient of the sphere varies with the color temperatures of a tungsten lamp.

ing proportional increase in the intensity of the violet and blue lines. This variability in the mercury arc is one of the reasons for the discordant results that are rather frequent in photometric literature.

The data here given lead to the conclusion that the true constant of the sphere can be obtained to within one-quarter of one percent, if the ratio R can be determined to within one-tenth of one percent. This accuracy is readily attained in laboratories accustomed to precision determinations, and repeated tests with the method confirm this computed accuracy for the sphere constant. (See Fig. 11.)

INTEGRATING FACTORS FOR VARIOUS LIGHT SOURCES

In addition to the tests on tungsten lamps already mentioned, a number of determinations have been made for the integrating factor when photometering several types of mercury arcs and other gaseous conductors.

The data in the last column of Table I show in an unmistakable manner that direct spherical photometry would benefit greatly by the development of a nonselective paint, and that in the meantime the Ulbricht sphere will bear study by the photometrist who seeks accurate data.

A Simplified Computation of Cartesian Lens Surfaces*

LUDWIK SILBERSTEIN, *Kodak Research Laboratories, Eastman Kodak Company, Rochester, N. Y.*

(Received July 27, 1935)

LET l_0 be the distance of the point-object O from the axial point P_0 of a Cartesian (aberration-free) surface, l the distance from P_0 of the image O' of O; further, μ and μ' the refractive indices of the media on the object and the image side, respectively, and x, y, the rectangular coordinates of any point P of the meridian curve of the Cartesian surface (a surface of revolution, of course), x being measured from P_0 along the axis towards O'. Then the equation of the meridian curve of the most general Cartesian surface, a quartic, can be written

$$\mu[(x-l_0)^2+y^2]^{\frac{1}{2}}+\mu'[(x-l)^2+y^2]^{\frac{1}{2}}=\mu l_0+\mu' l. \quad (1)$$

The procedure, for the grinding workshop, hitherto used at the Hawk-Eye Works of the Eastman Kodak Company, consisted in developing x into a power series of y. This, however, has entailed a rather laborious computation resulting in a cumbersome numerical table.

The purpose of the present paper is to give a much simpler method of computation. The simplifying artifice of this method consists in comparing the quartic curve (1) with its *curvature circle* at the axial point $x=0$ and, ultimately, evaluating the difference of the abscissae of the curve and the circle corresponding to the same ordinate y, say

$$\Delta x=x-x_c, \quad (2)$$

where x_c is the abscissa of a point on the circle.

Let ρ be the curvature of the circle. Then its equation is

$$(x_c-1/\rho)^2+y^2=1/\rho^2, \quad (3)$$

if the Cartesian surface is assumed to be convex towards the object O. This gives

$$x_c=(1/\rho)\{1-(1-\rho^2y^2)^{\frac{1}{2}}\}$$

or, developed into a power series of y^2, with $\rho y<1$,

$$x_c=-\frac{1}{\rho}\left\{\frac{1}{2}\rho^2y^2+\frac{1}{8}\rho^4y^4+\frac{1}{16}\rho^6y^6+\frac{5}{128}\rho^8y^8+\dots\right\}. \quad (4)$$

On the other hand, the Cartesian curve (1) being symmetrical with respect to the axis (and $x=0$ for $y=0$), we have the Taylor series

$$x=x_0'y^2+\frac{x_0''}{2!}y^4+\frac{x_0'''}{3!}y^6+\dots,$$

where $x'=dx/d(y^2)$, and the subscript $_0$ denotes the value of x, etc., for $y=0$, i.e., at P_0. Now, the absolute value of the curvature of the Cartesian curve is, at any point

$$|(d^2x/dy^2)/[1+(dx/dy)^2]^{\frac{3}{2}}|,$$

where $dx/dy=2yx'$ and $d^2x/dy^2=2x'+4y^2+x''$, x' being defined as above. Thus, the curvature at P_0 is simply

$$\rho=|2x_0'|=2x_0',$$

since x_0' is positive (curve convex towards O).

Consequently, the last written series form of the equation of our curve becomes

$$x=\frac{1}{2}\rho y^2+\frac{x_0''}{2!}y^4+\frac{x_0'''}{3!}y^6+\cdots. \quad (5)$$

The first term is exactly as in (4), so that the required difference of abscissae of corresponding points of the Cartesian curve and the circle is

$$\Delta x=\left(\frac{x_0''}{2}-\frac{1}{8}\rho^3\right)y^4+\left(\frac{x_0'''}{6}-\frac{1}{16}\rho^5\right)y^6+\left(\frac{x_0^{IV}}{24}-\frac{5}{128}\rho^7\right)y^8+\cdots. \quad (6)$$

The lowest term is of the *fourth* order in y, the height. To determine the coefficient of this term as well as the coefficients of y^6, etc., it suffices to evaluate x_0'', x_0''', etc. Now, differentiating the Eq. (1) of the Cartesian curve with respect to $u=y^2$, we have, for any y,

$$\mu\frac{1+2(x-l_0)x'}{[(x-l_0)^2+u]^{\frac{1}{2}}}+\mu'\frac{1+2(x-l)x'}{[(x-l)^2+u]^{\frac{1}{2}}}=0, \quad (7)$$

whence $2x_0'=\rho=(\mu/l_0+\mu'/l)/(\mu+\mu')$. (8)

* Communication No. 547, Physics Department, Research Laboratories, June 3, 1935.

Differentiating (7) once more with respect to u and putting $u=0$, one finds, after substitution of $x_0'=\rho/2$,

$$x_0''=\frac{1}{\mu+\mu'}\left[\left(\frac{\mu}{l_0^2}+\frac{\mu'}{l^2}\right)\frac{\rho}{2}-\frac{1}{4}\left(\frac{\mu}{l_0^3}+\frac{\mu'}{l^3}\right)\right], \quad (9)$$

which is the required constituent of the coefficient of y^4 in formula (6).

Thus, the difference Δx is, up to the *sixth* order in y,

$$\Delta x=\frac{1}{4}\left\{\frac{(\mu/l_0^2+\mu'/l^2)\rho}{\mu+\mu'}-\frac{1}{2}\left(\frac{\mu}{l_0^3}+\frac{\mu'}{l^3}\right)-\frac{1}{2}\rho^3\right\}y^4, \quad (10)$$

where, as before,

$$\rho=(\mu/l_0+\mu'/l)/(\mu+\mu').$$

This result is valid for *any* Cartesian surface, convex towards the object, namely, for *any* pair of media (μ, μ') and any position of the object O, i.e., for any value of l_0.

For $l_0=\infty$ (parallel-beam of incident rays) we have $\rho=\mu'/(\mu+\mu')l$, so that (10) reduces to

$$\Delta x\doteqdot-\frac{\mu^2\mu'}{8(\mu+\mu')^3l^3}y^4=-\frac{1}{8}\left(\frac{\mu}{\mu'}\right)^2\rho^3y^4, \quad (10a)$$

where ρ is the curvature of the surface at the axial point. In this particular case the meridian curve of the surface is (as is well known) an ellipse, to wit, of eccentricity $\epsilon=\mu/\mu'$. From the sign in (10a) we see that the curvature circle touches the Cartesian meridian curve on its concave face, if the surface is convex towards the object.

To illustrate this result by a concrete example, we may consider $\mu=1$, $\mu'=1.5$. Then, writing R for the curvature radius $(1/\rho)$ at the axial point,

$$\Delta x\doteqdot-(1/18)(y/R)^2y,$$

e.g., for $y=R/10$

$$\Delta x\doteqdot-R/180{,}000,$$

and for $y=R/5$, $\Delta x\doteqdot-R/11{,}250$. Thus, the Cartesian surface is seen to deviate from the osculating sphere at P_0 very little indeed, even at the relatively considerable height $y=R/5$, always up to y^6 and higher terms. Whence it can be readily surmised that the sixth-order term will be practically negligible. In spite of this, it has seemed worth while to evaluate this term, i.e., $(x_0'''/6-\rho^5/16)y^6$, as in (6). Differentiating Eq. (7) twice with respect to y^2, putting $y=0$, and substituting $x_0'=\frac{1}{2}\rho$, one finds

$$\begin{aligned}x_0'''=\frac{1}{\mu+\mu'}\Bigg\{&\frac{3}{8}\left(\frac{\mu}{l_0^5}+\frac{\mu'}{l^5}\right)\\&-\frac{3}{8(\mu+\mu')}\left(\frac{\mu}{l_0^2}+\frac{\mu'}{l^2}\right)\left(\frac{\mu}{l_0^3}+\frac{\mu'}{l^3}\right)\\&+\frac{3}{4}\left(\frac{\mu}{l_0^2}+\frac{\mu'}{l^2}\right)\frac{\rho}{\mu+\mu'}-\frac{9}{8}\left(\frac{\mu}{l_0^4}+\frac{\mu'}{l^4}\right)\rho\\&+\frac{3}{4}\left(\frac{\mu}{l_0^3}+\frac{\mu'}{l^3}\right)\rho^2\Bigg\}. \quad (11)\end{aligned}$$

This holds for any Cartesian surface (always convex towards the object). A substitution in $(x_0'''/6-\rho^5/16)y^6$ gives the required sixth-order term of Δx.

For the particular case $l_0=\infty$ the last formula is considerably simplified, namely, to

$$x_0'''=\tfrac{3}{8}(1-2n^2+n^4)\rho^5/n^4, \quad (11a)$$

where $n=\mu'/\mu$. Thus, the coefficient of y^6 in the series for Δx becomes

$$\frac{x_0'''}{6}-\frac{\rho^5}{16}=\frac{1-2n^2}{16n^2}\rho^5.$$

This expression, multiplied by y^6, is to be added to the fourth-order term as given in (10a). Thus, up to y^8 the required deviation of the Cartesian surface from its central osculating sphere is

$$\Delta x\doteqdot\frac{\rho^3y^4}{8n^2}-\frac{2n^2-1}{16n^4}\rho^5y^6, \quad n=\frac{\mu'}{\mu}. \quad (12)$$

If, e.g., $n=3/2$, as in the previous example, then

$$\Delta x\doteqdot-\frac{1}{18}\left(\frac{y}{R}\right)^3y\left[1+\frac{7}{9}\frac{y^2}{R^2}\right].$$

The ratio of the sixth- to the fourth-order term is

$$C_6:C_4=(7/9)(y/R)^2,$$

e.g., for $y=R/10$, $C_6:C_4=7/900$ only.

For most practical cases, then, the fourth-order term alone is all that need be considered.

A Photoelectric Colorimeter with Logarithmic Response*

RALPH H. MÜLLER AND GILBERT F. KINNEY, *Department of Chemistry, Washington Square College, New York University*

(Received May 17, 1935)

The instrument consists of a vacuum photoelectric cell feeding into a vacuum tube voltmeter with logarithmic input characteristic. The voltmeter employs a type 6D6 tube which is provided with a properly chosen biasing resistor in the cathode lead. This gives a plate current proportional to the logarithm of the input voltage. Since this relationship never extends to zero plate current, a portion of the plate current is balanced out, giving in effect, a suppressed zero instrument. Suitable shunts and a choice of input resistors afford several ranges of sensitivity. The output meter can be calibrated directly in concentration units. Other methods of achieving the same result are discussed.

INTRODUCTION

THE trend in modern objective colorimetry is undoubtedly in the direction of methods embodying rigorous physical principles and the elimination of purely empirical procedures. The photoelectric method of comparing colored solutions for the purpose of quantitative chemical analysis can be arranged to conform to the requirements of the Lambert-Beer law.

$$I = I_0 e^{-kct}, \tag{1}$$

where I_0 and I are the intensities of the incident and transmitted beams, c, the concentration of absorbing solute, and t, the depth of absorbing layer.

For an absorption cell of constant thickness and with monochromatic light, or at least a fairly restricted range of wave-lengths, the relationship can be used in the form

$$\log (I_0/I) = k'c. \tag{2}$$

Fig. 1 shows convenient modes of representing the results. It is assumed that I_0 is held constant, and in (2) by the use of semilogarithmic coordinates, the concentration of the absorbing substance is represented simply and conveniently. Either of these methods is rigorous and suited to the requirements of precise colorimetric analysis.[1]

There is a great advantage, however, in having an instrument which can be calibrated directly and with linear scale in concentration units. This is particularly desirable for routine work and for automatic recording in that it eliminates all calculation or plotting of curves. Since the transmitted light is a logarithmic function of the concentration, we can obtain direct readings by using a circuit which possesses logarithmic response. A device of this kind is logarithmic vacuum tube voltmeter.[2]

After our paper was read, an article by C. W. Miller entitled *A Linear Photoelectric Densitometer* was published (Rev. Sci. Inst. **6**, 125 (1935)). It is difficult to evaluate the instrument since no data are given by the author. The single curve shown reveals a gross logarithmic response with apparent deviations from the desired relationship as high as 25 percent. It is not apparent how anything short of empirical calibration over the whole scale would render it useful for precise measurement. In addition the author states, p. 127, "The instrument, may, of course, be used in a similar fashion for colorimetric observations, but the logarithmic character of its response would not seem to possess so great an advantage for this work." This char-

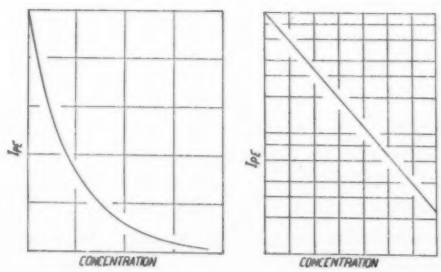


FIG. 1. Modes of representing colorimetric data.

* Read at the New York Meeting of the Optical Society of America, February 23, 1935.

[1] R. H. Müller, Mikrochemie **11**, 353 (1932); Ind. Eng. Chem. Anal. Ed. **7**, 223 (1935).

[2] S. Ballentine, Electronics **2**, 472 (1931); J. Acous. Soc. Am. **5**, 10 (1933); F. V. Hunt, R. S. I. **4**, 672 (1934).

acteristic, if it can be achieved, is of tremendous advantage in colorimetry and is the basis of the present work.

Logarithmic Vacuum Tube Voltmeter

The voltmeter has an output current varying linearly with the logarithm of the input voltage, and depends on the plate current-grid voltage relationship of a variable mu ("super-control") type of vacuum tube. When a tube of this type is operated with negligible resistance in the output circuit, the plate current increases, over a certain range, more rapidly with increasing grid voltage than would be the case if a strictly logarithmic relationship were followed; on the other hand, with a high load resistance the increase in plate current is less rapid than desired. It is, therefore, possible to choose load conditions to give the desired characteristic. (Hunt[2] uses a diode for this plate load resistance, utilizing its peculiar voltage-current relationship to extend the logarithmic characteristic as well as to rectify the amplified alternating current to be measured.) Since resistance in the circuit introduces losses, it is advisable to use, if possible, small values. Therefore the resistance is transferred from the plate circuit to the cathode circuit, where its leveling action is enhanced by its effect in the control grid voltage.

The choice of this resistance is made from the curves shown in Fig. 2, where the grid voltage (input) is plotted on a logarithmic scale against plate current (output). With these coordinates the desired characteristic is a straight line, and this condition can be obtained so that it extends over practically the entire useful range of quantitative colorimetry. (For the sake of clarity, these curves are staggered along the plate current axis, otherwise they are practically superimposed at low values of plate current where the effect of added resistance is small.)

The region of linearity, as shown by the plot, never extends to zero plate current. For this reason it is desirable to use as a measuring instrument a meter with suppressed zero; this effect can be realized by balancing out a portion of the plate current. Such an arrangement permits the use of a sensitive meter and so affords greater precision and sensitivity, which, of course, cannot be extended indefinitely. A natural limit is set by random fluctuations in photo-

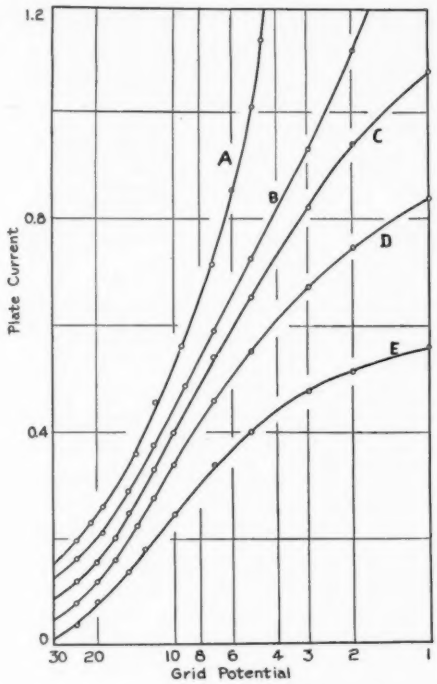


Fig. 2. Plate current-grid potential values as a function of cathode resistance. $A=0\Omega$, $B=1800\Omega$, $C=2500\Omega$, $D=5000\Omega$, $E=10{,}000\Omega$.

electric and thermionic emission. In this instrument, even though a substitution method is employed, rapid and sudden changes in the light source probably constitute the actual limit of the sensitivity obtainable.

The complete circuit is shown in Fig. 3. The photoelectric cell is a General Electric PJ–22 vacuum cell.* The input resistance, R_1, can be chosen by the selector switch, S_1, to be three, ten, or fifty megohms. Higher values, while desirable from a sensitivity point of view, are impracticable because of the small but finite grid current in the tube. The photo-cell battery, B_1, is large enough to provide saturation voltage for the photoelectric cell at the prevailing light intensities even after the drop in resistor, R_1, is deducted. Ninety volts has proven satisfactory. R_2 is the important cathode resistor. It must be

* Other cells, if available, might perhaps be more sensitive.

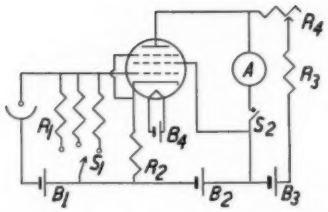


FIG. 3. Circuit for logarithmic photoelectric colorimeter.

chosen with a particular tube to give the proper characteristic (Fig. 2), its value being generally between two and three thousand ohms. The vacuum tube is an R.C.A. type 6D6, chosen for its variable mu characteristic and for its general excellent construction, which with its low heater to cathode leakage and low grid current gives unusually stable operation for a tube with six elements. Plate and screen voltages for the tube are both supplied by one forty-five volt battery, B_2. B_3, together with R_3 and R_4, give the meter its suppressed zero characteristic. B_3 is one cell (2 volts) of the six-volt storage battery which supplies the heater of the tube and the automobile headlight bulb used as the source of light. R_4 permits compensation for drift, aging, and slow changes in the circuit; R_3 is a protective resistor to prevent accidental application of the full voltage on the meter. The meter is a multirange microammeter with mirror scale. It is connected in the circuit through the nonlocking switch, S_2, which is used only when a reading is made. Keeping the meter out of the circuit at all times avoids accidental overloading.

COMPLETE COLORIMETER

The principal mechanical and optical features of the instrument are shown in Fig. 4(a). The optical assembly consists of an automobile headlight source, S, a spherical mirror, M, and a short focus lens, L, supplying a parallel beam of light. A Corning filter, F, admits those wavelengths corresponding as nearly as possible to the absorption maximum of the solution.*

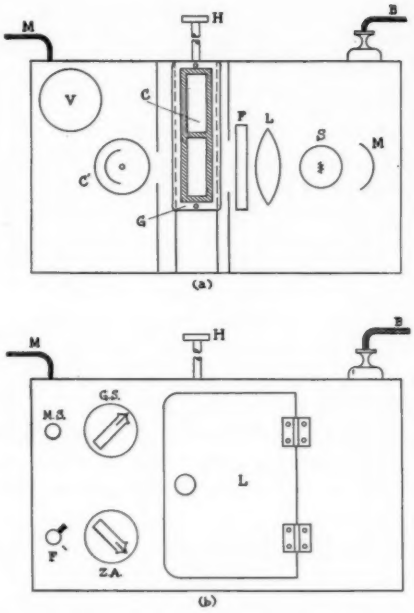


FIG. 4. Mechanical disposition of parts in completed colorimeter.

The beam enters one of the compartments of the twin absorption cell, C. The latter consists of two plane parallel glass cells, the bases of which are cemented to an aluminum plate. This plate is provided with two small holes which fit steel pins in the movable slide, G. The twin cell can be lifted from the pins for the purpose of cleaning and filling. Handle, H, permits the cell assembly to be moved laterally across the optic axis. Suitably positioned stops limit the motion of the cell carrier, assuring accurate centering of either cell in the light beam. The photo-cell and vacuum tube are designated as C' and V, respectively. Cable B, fitted with a six-prong adaptor, provides all battery connections, and cable M connects the multirange microammeter. The colorimeter housing is made of sheet aluminum; the interior is painted dead-black. Fig. 4(b) shows the top of the case. The hinged lid, L, permits access to the absorption cells and filter. "G.S." is the grid resistance selector switch (S_1 in Fig. 3)

* No attempt will be made here to discuss the conditions under which Beer's law is obeyed for the given system. This has been treated in many texts and individual papers. (See reference 1.) Since the present instrument is based on rigid conformity with the law, it will be evident that we are concerned only with those systems which have been carefully studied from the physico-chemical and optical point of view.

and "Z.A." the zero adjustment (R_4 in Fig. 3), F is the vacuum tube filament switch, and "M.S." is the nonlocking push button connecting the meter to the circuit.

Performance

To illustrate how well the instrument functions, some representative measurements are given for the colorimetric determination of copper. (Extensive analyses which have been made by the instrument will be published elsewhere.) Standard solutions containing copper at various concentrations were treated with ammonium nitrate and excess ammonia and diluted accurately to the mark in a volumetric flask. The resulting blue solutions were photometered in the instrument. Three individual samples at each concentration were measured to provide checks. This system, with the appropriate filter, has been shown in this laboratory to follow Beer's law very accurately up to a concentration of 1200 mg/liter (approx. parts per million). Fig. 5 shows the plate current plotted against concentration. The desired linear relationship is obeyed very closely.

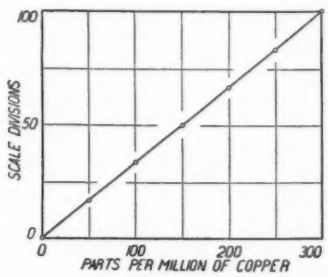


FIG. 5. Photoelectric measurements with copper solutions, illustrating logarithmic (direct reading) response.

TABLE I.

CONCENTRATION OF COPPER TAKEN (parts per million)	CONCENTRATION FOUND (average of three determinations)
50.0	49.7±0.2
100.0	100.6±0.5
150.0	150.0±0.7
200.0	200.0±0.3
250.0	249.5±0.4
300.0	300.0±0.5

One-fifth scale division equals 0.6 parts per million.

Table I gives a set of representative measurements. If the average slope is calculated, subsequent measurements can be interpreted by multiplying the observed current by the reciprocal of the average slope. For routine measurements the meter shunt can be chosen so that the scale reads concentration or percent of a desired constituent directly.

Alternative Methods

There are several ways of achieving the desired logarithmic response among which optical compensation with a wedge is an obvious solution. Since we have been concerned only with electrical methods it may be of interest to record our observations on barrier-layer cells. Fig. 6 shows the relation between the open circuit e.m.f. of a Photronic cell and the light intensity. We have preferred to use the data given in the *Weston Instrument Company Bulletin*, although we have confirmed it repeatedly on numerous cells. The precise logarithmic behavior above a certain level of illumination is evident.†

The circuit shown in Fig. 7 is satisfactory for the photometry of solutions. The slider is placed at point A for the initial condition, i.e., when the colorimeter cup containing pure solvent is in position. Resistor R_2 is then adjusted until galvanometer, G, indicates balance. The introduction of the cup containing colored solution

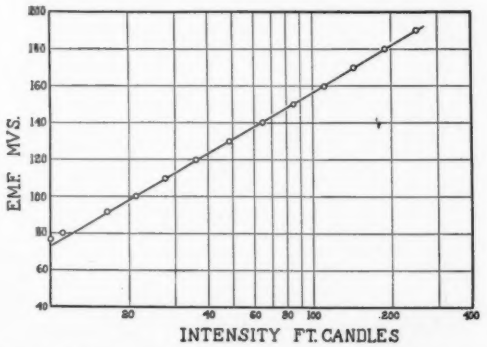


FIG. 6. Logarithmic response of Weston Photronic cell.

† A comprehensive theoretical treatment of the barrier-layer cell recently completed by A. Spector in this laboratory predicts the logarithmic behavior. Details will appear in the near future in Phys. Rev.

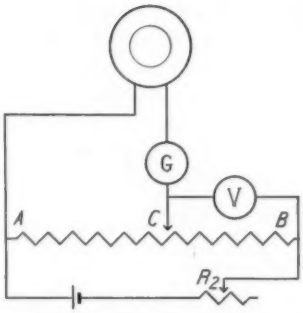


FIG. 7. Circuit for logarithmic colorimeter employing a Photronic cell.

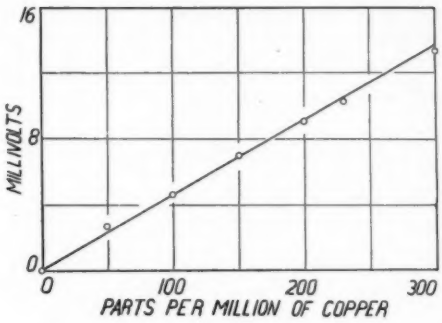


FIG. 8. Photoelectric measurements with copper solutions, using circuit shown in Fig. 7.

decreases the light intensity and the slider, C, will now have to be moved to the left to reestablish balance. The potential difference indicated by V is proportional to the concentration. The position chosen for V is occasioned by the desirability of having the potential *readings* increase with increasing concentration, rather than decrease.

In Fig. 8 some measurements on copper solutions are recorded. We have not completed various obvious refinements of the circuit and, therefore, cannot state how this method compares in precision with the vacuum tube voltmeter. The Photronic cell has been used for several years in this laboratory for colorimetry by measuring the short circuit current and under these conditions has yielded excellent results. The above described variation seems to offer an interesting and useful instrument.

CONCLUSION

The logarithmic vacuum tube voltmeter which has been developed to measure photoelectric currents in a photometer possesses advantages which are of particular use in the measurement of colored solutions. Many physico-chemical expressions involve logarithmic terms and wherever direct reading is desirable, the device should prove useful. A few instances are pH values and the electromotive force of concentration cells. In some cases it would be desirable to add a linear amplifier to secure a larger output and permit the use of a more robust indicating meter.

Apparatus for Darkfield Photometry and Densitometry*

P. S. WILLIAMS AND GORDON H. SCOTT, *Anatomical Laboratories, Washington University School of Medicine, St. Louis*

(Received June 7, 1935)

IN consequence of work in this laboratory on the emission spectrography of biological materials,[1] the need was felt for a simple and serviceable densitometer capable of measuring the blackness of the narrow spectral lines given by the small spectrograph (a Gaertner L 250W) used. Other work on nuclear salts required a darkfield photometer for measuring the light scattered from ash deposits on very small areas of incinerated tissue sections as described by Scott.[2] It has been possible to design and construct a very satisfactory assembly, convertible in two or three minutes from one use to the other. Since it makes use chiefly of parts to be found in many laboratories and involves only elementary shopwork, it may be of interest to others needing either or both instruments.

The arrangement consists essentially of a permanently mounted microprojection system, the images from which are focused on one or the other of two interchangeable photo-cell boxes. One of these is designed for the densitometry application, the other for darkfield photometry.

The whole assembly, with the latter box in place, is shown in Fig. 1, set up in a small darkroom. The lamp and scale for the Leeds and Northrup type *R* galvanometer is on the shelf. On the table, from left to right: A constant-voltage transformer and step-down transformer; the ventilated wooden box housing the 6-v, 108-watt ribbon filament projection lamp; the microscope assembly; and the photo-cell box, the amplifier cabinet for which is under the table.

The microscope has a Zeiss aplanatic 1.2 condenser, a Leitz number 3 objective, various oculars, and a clamped-on 90° reflecting prism.

The fixed (circular) diaphragms were made interchangeable, and slip into the condenser lens ring. That for the densitometric work restricts the cone of light delivered by the condenser to that taken up by the objective, in order to reduce light scattering from the plate emulsion; to further approach this object, and to reduce scattering and chromatic aberration in the whole optical system, this diaphragm carries also a Wratten 22 (brownish-red) color filter. The darkfield diaphragm is simply a disk very slightly larger than the aperture in the above, and carries no color filter. The mechanical stage for the plate or slide gives rack-and-pinion adjustments laterally and vertically and a fine screw adjustment axially; the latter feature had to be built specially. The whole arrangement is carried by the microscope frame, the stage having been removed to increase clearances.

Details of the two cell boxes are shown in Fig. 2. The densitometry box, at the left, contains a Weston Photronic cell under an adjustable-

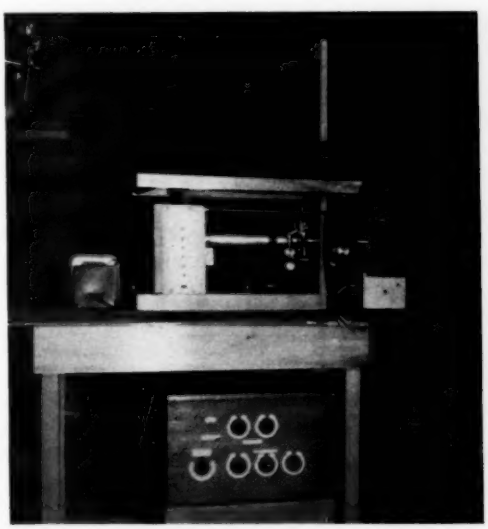


FIG. 1. Over-all view of assembly showing darkfield photocell box in position.

* Aided by grants from the Macy Foundation, an appropriation from a grant made by the Rockefeller Foundation to Washington University for research in science, and the International Cancer Research Foundation.

[1] Gordon H. Scott and P. S. Williams, Proc. Soc. Exper. Biol. and Med. **32**, 505 (1935).

[2] Gordon H. Scott, Proc. Soc. Exper. Biol. and Med. **30**, 1304 (1933).

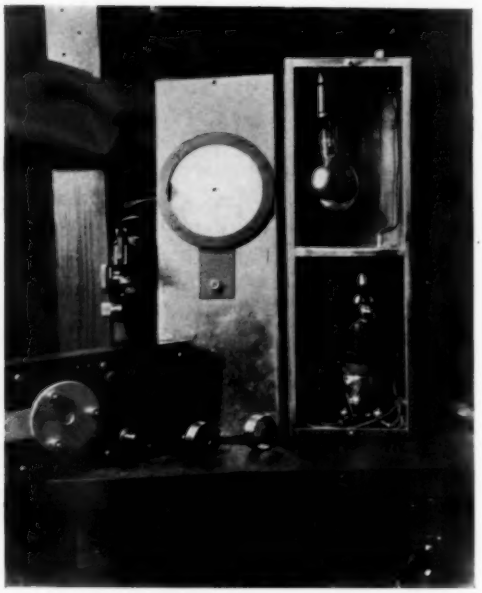


FIG. 2. Details of photo-cell boxes and diaphragms.

width aluminum slit with sliding shutter. It also contains a short-circuiting switch for the cell, a 10,000-ohm rheostat in series with the cell and the phone jack sockets for connecting the galvanometer, the damping of which is controlled by the rheostat.

At the right is the cell box for the darkfield work with cover standing beside it. The box, of heavy copper, is light-tight and gives good electrostatic screening. The photoelectric cell (top) is directly connected to an FP54 Pliotron (bottom); the 10^9-ohm high resistance shunt is in the shadow. The connections to the amplifier,* photo-cell *B* battery, etc., run to the cabinet through a flexible shielded cable, which also brings the galvanometer leads back to phone sockets on the box. The same galvanometer is used then with either pick-up assembly. The cover of the box carries the rotatable and interchangeable 3″ white cardboard disks serving as slits; any size and shape aperture falling within a 3/4″ circle may be used. The sliding shutter works under these.

USE AS DENSITOMETER

With the spectrographic plate in the stage, the prism reflecting downward, the proper diaphragm and usually a 10× ocular (giving 64× magnification), the barrel of the microscope is adjusted and the photronic cell box is moved about on the table so that the slit is centrally and symmetrically placed in a clear-cut image of the ribbon filament of the lamp. The slit is 13×0.8 mm, the image 17×4.5, so this latter is not difficult. Both the microscope and the cell box then remain fixed. By using the three stage adjustments, the center of the line of interest is focused over the slit; the galvanometer deflection which occurs when the shutter is pulled is then proportional to the light transmitted through the line. This, with the deflection for an unexposed portion of the plate, yields the density of the line. The ~0.8 mm slit width is set to give nearly full scale clear plate deflection.

USE AS A DARKFIELD PHOTOMETER

The arrangement to be described is that used for measuring scattered light from the mineral residues left by incinerated nuclei of single cells. Naturally the previously used magnification of 64 is insufficient. The reflecting prism is turned 180° and the light from the (15×) ocular reflected up to the mirror (Fig. 1, upper right) and back down to the cardboard disk on the lid of the copper photoelectric cell box, which replaces the small photronic cell box used above. This raises the magnification to 700, with which the diameter of the image of a nuclear area is of the order of 1/4″.

The first step is as before to focus the filament image sharply and centrally on the cardboard screen; this is done with neither diaphragm in place and with the ash-bearing glass slide in position. It is convenient to increase the size of the filament image to about 4″ in width by putting a 12-power convex lens in front of the lamp housing. These adjustments are made but once. Then the darkfield diaphragm is inserted and, with all the felt curtains down and the room almost completely dark, the image of the ash

* The amplifier circuit is that described by DuBridge and Brown (Rev. Sci. Inst. **4**, 532 (1933), using 12 v of lead cells.

deposits is focused on the screen with the axial adjustment of the stage. The image is faint but sufficiently visible. The portion to be measured is brought close to the center of the screen using the stage adjustments; the precise setting of the aperture in the screen is made by moving the cell box itself. The galvanometer deflection, when the shutter is pulled, is proportional to the scattered light passing through the aperture. The 'background' is not completely dark, so that it is necessary to subtract the small clear slide deflection from the above to get the light scattered by the ash itself. The resulting number is more or less proportional to the amount of ash (if small) on the area taken, and can be compared with a similar measure for another area of the slide without concern as to the actual amounts of ash involved.

With 700 magnification, the 1/10 galvanometer shunt, and a 1/4″ aperture in the screen, about half-scale net deflection is obtained from the ash due to a 5μ section through a single nucleus.

Remarks

The inherent flexibility of the apparatus, in regard to magnifications, uses, etc., is obvious, and only the configurations usually employed in this laboratory have been given in detail. However, two points of interest should be noted. The first is that the use of a lower (than 10×) ocular, or none at all, in the densitometer increases the intrinsic brightness of the filament image in proportion to the diminution in its area; this makes it possible to accurately measure the density of a very black line, so long as its image is wide enough to cover the slit with the lower magnification. The clear plate deflection under these circumstances can be arrived at through measurements on an area of intermediate blackness with both magnifications. The second point is that the darkfield arrangement should be serviceable for measuring very *faint* traces on photographic plates. The magnification, slit aperture, etc., would depend on what was being measured.